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^{15}N Nuclear Magnetic Resonance Spectroscopy. Products and Rearrangements in the Reaction of *p*-Toluenesulfonyl Azide-*3*-^{15}N with the Sodium Salt of *p*-Toluenesulfonamide. An in Situ ^{15}N NMR Study[1]

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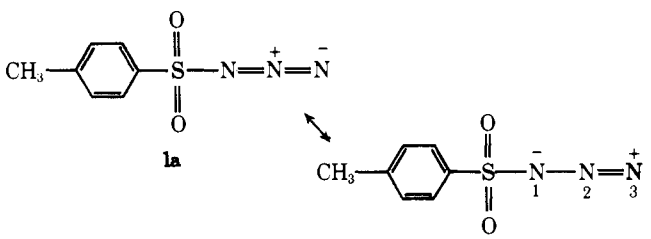
Abstract: The formation of isotope-scrambled ^{15}N-labeled diazocyclopentadiene from the reaction of *p*-toluenesulfonyl azide-*3*-^{15}N (**1**-*3*-^{15}N) with cyclopentadiene is caused by one of the reaction products (*p*-toluenesulfonamide anion) which is quite effective for scrambling **1**-*3*-^{15}N. A number of concurrent reactions of **1**-*3*-^{15}N with the sodium salt of *p*-toluenesulfonamide in dimethyl sulfoxide were followed by ^{15}N NMR. **1**-*2*-^{15}N is formed as a result of a degenerate diazo transfer by **1**-*3*-^{15}N to *p*-toluenesulfonamide anion. *p*-Toluenesulfonamide anion also reacts with **1**-*3*-^{15}N to give di-*p*-toluenesulfonamide and azide ion. The ^{15}N-labeled azide ion exchanges with **1** to give **1**-*1*-^{15}N. **1** also reacts with azide ion, yielding dinitrogen and *p*-toluenesulfinate anion. The sulfinate salt reacts readily and reversibly with **1** to give 1,3-di-*p*-toluenesulfontriazene anion, which provides another pathway for interconversion of **1**-*3*-^{15}N and **1**-*1*-^{15}N.

Introduction

p-Toluenesulfonyl azide (**1**) is a highly versatile and useful reagent[2] which, depending on the conditions, can behave as an electrophile, nucleophile, a 1,3 dipole,[3] or source of *p*-toluenesulfonylnitrene.[3] As an electrophile, **1** resembles aryldiazonium compounds. The electrophilic nature of N3 (the terminal nitrogen) can be rationalized by the resonance structure **1b** and is exploited in the well-known diazo[4] and azido[5]



1a ↔ **1b**

transfers to active methylene groups. These transfers are believed to occur by the mechanistic steps of Scheme I.[4,6] The carbanion formed by ionization of the substrate attacks the electrophilic N3 of **1** to give a triazene adduct, **2**. Such triazenes have occasionally been isolated and characterized.[6,7] When the anion has an α hydrogen (R′ = H), **2** tautomerizes to **3**, and **3** then decomposes to yield a diazo compound and the resonance-stabilized *p*-toluenesulfonamide anion. When the anion has no α hydrogen (R′ ≠ H), **2** decomposes directly to give an azido compound and *p*-toluenesulfinate anion. Both diazo and azido transfers by **1** have, in recent years, been extended to a wide variety of nitrogen anions, primarily by Anselme and co-workers.[8,9]

Recently, **1** labeled at N3 with ^{15}N was used to synthesize labeled diazocyclopentadiene, and, contrary to expectations, the ^{15}N NMR spectrum of the product showed that, in addition to **4**, about 5% of **5** was formed.[10] The discovery by several research groups[11,12] that **1** transfers a diazo group to the magnesium salts of primary amines by the process of eq 2[11] suggests that **1**-*3*-^{15}N might be scrambled by the *p*-toluenesulfonamide anion formed in eq 1 as the result of a degenerate diazo-transfer reaction.

In this paper, we give an account of the reactions of **1**-*3*-^{15}N with the sodium salt of *p*-toluenesulfonamide (generated in situ from excess *p*-toluenesulfonamide) in dimethyl sulfoxide,

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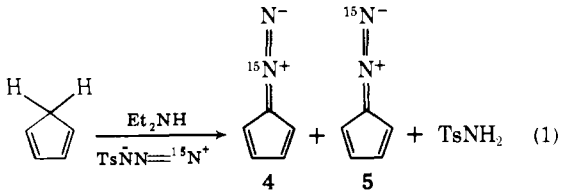
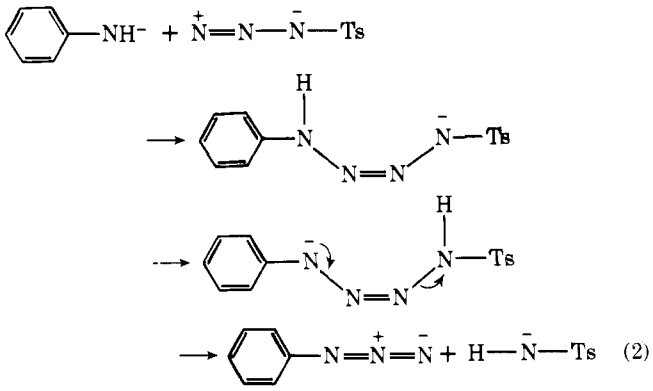
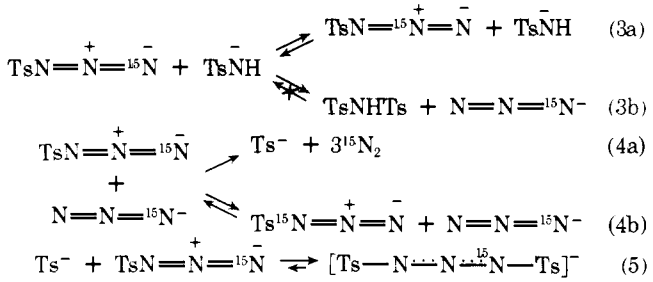




as observed by ^{15}N NMR. Strong evidence was obtained by ^{15}N NMR for each of the reactions shown by eq 3-5.



Results and Discussion

The ^{15}N spectra of **1**-*3*-^{15}N in the presence of the sodium salt of *p*-toluenesulfonamide, in dimethyl sulfoxide, show that **1** is completely scrambled and, in addition, many new ^{15}N-labeled products are formed (see Figure 1). The ^{15}N resonances at 234.2, 142.0, and 132.1 ppm correspond to ^{15}N labels at the N1, N2, and N3 positions of **1**, respectively.[10]

Formation of 1-*2*-^{15}N. The ^{15}N label at N2 of **1** must arise via a fast[13] degenerate diazo transfer by **1**-*3*-^{15}N to *p*-toluenesulfonamide anion through the intermediacy of the sulfontetrazene[14] anions, **6**.

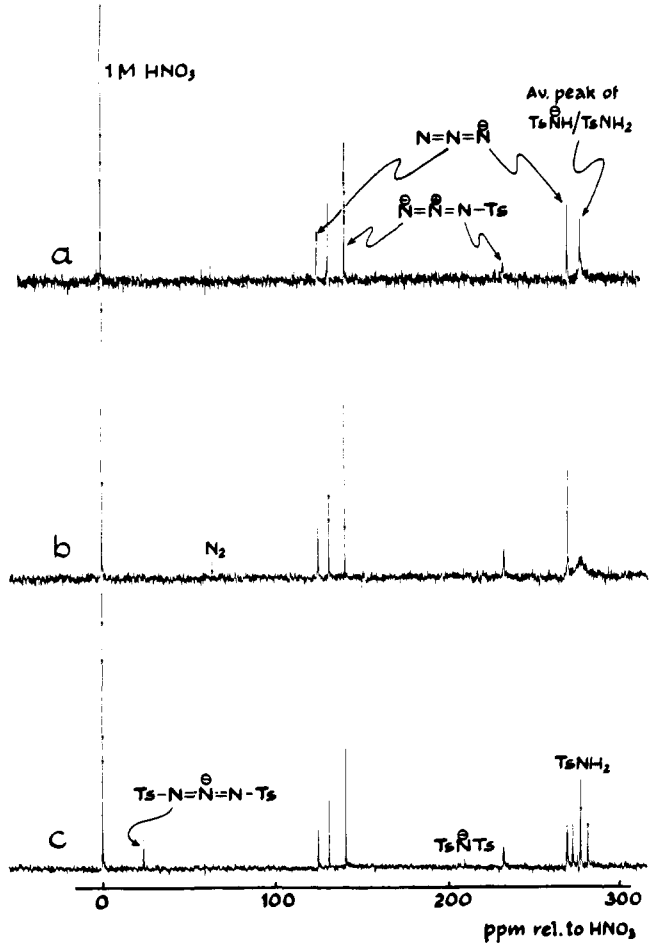
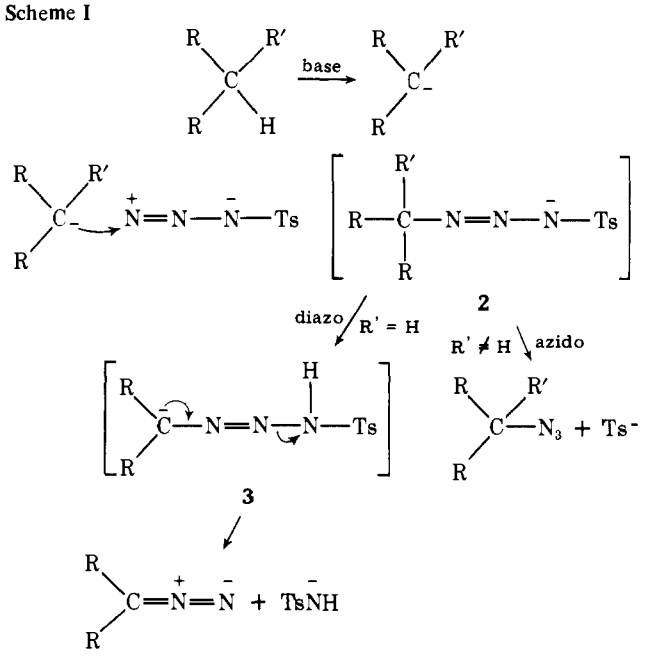
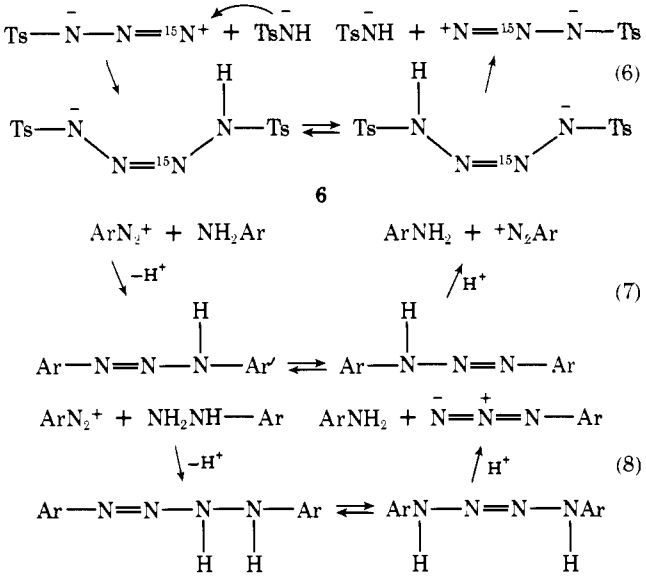


Figure 1. ^{15}N spectra of 5.0×10^{-3} mol of sodium salt of *p*-toluenesulfonamide ($TsNH^-$), 5.0×10^{-3} mol of *p*-toluenesulfonamide ($TsNH_2$), and 8.1×10^{-3} mol of *p*-toluenesulfonyl azide-*3*-^{15}N ($^{15}N^-{=}N^+{=}NTs$) in 20 mL of dry dimethyl sulfoxide; 20-μs pulse angle, 10-s repetition rate. Spectrum of sample (a) 10 min after preparation, 410 transients; (b) 5 h after preparation, 1015 transients; (c) 78 h after preparation, 1654 transients.

Scheme I





The reaction of eq 6 parallels the reactions of aryldiazonium salts with amines but, because diazonium salts are more

nucleophilic than **1**, the amine need not be in the form of the conjugate base, as in eq 6. The diazo migration[15] (eq 7) and the coupling of an aryldiazonium salt with an arylhydrazine[16] (eq 8) are examples of such reactions.

The scrambling of **1**-*3*-^{15}N by the equilibrium of eq 6 could easily account for the small amount of **5** formed when **1**-*3*-^{15}N reacts with cyclopentadiene. Because diethylamine catalyzes the ionization of cyclopentadiene ($pK_a \sim 15$)[17] in the first step of the diazo transfer,[3,18] it must certainly be able to convert *p*-toluenesulfonamide ($pK_a = 10.3$)[19] to its conjugate base to at least some extent.

Formation of Di-*p*-toluenesulfonamide. The resonances at 271.5 and 125.8 ppm in Figure 1 arise from sodium azide-*1*-^{15}N and sodium azide-*2*-^{15}N, respectively.[20] The azide ion results from nucleophilic attack[21] by *p*-toluenesulfonamide anion on the sulfonyl sulfur of **1**.[22] Control experiments in dimethyl sulfoxide show that eq 9 is not appreciably reversible. We suspect that strongly acidic[23] di-*p*-toluenesulfonamide (**7**) protonates the azide ion and thereby inhibits the reverse reaction. In the reaction mixture of Figure 1, however, the strongest base is *p*-toluenesulfonamide anion, and the following proton exchange occurs. The reaction of eq 10 has been verified by ^{15}N NMR.

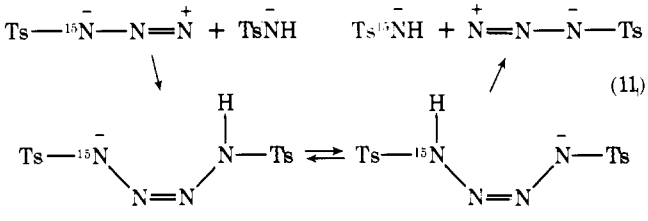
$$TsN_3 + TsNH^- \rightleftharpoons TsNHTs + N_3^- \quad (9)$$

$$TsNHTs + TsNH^- \rightarrow TsNTs^- + TsNH_2 \quad (10)$$

Equations 9 and 10 can account for the gradual transformation of the singlet at 279 ppm (Figure 1a) to the triplet at 279 ppm[24] (Figure 1c). The singlet in Figure 1a arises from *p*-toluenesulfonamide in equilibrium with a small amount of *p*-toluenesulfonamide anion (only one peak is observed because of fast proton exchange). In Figure 1c (~80 h after sample preparation) all of the anion is consumed and only *p*-toluenesulfonamide remains so that a triplet results. The resonance of the anion of the strongest acid, di-*p*-toluenesulfonamide, is now visible at 211.6 ppm, and this anion is not basic enough to exchange rapidly with *p*-toluenesulfonamide.

Formation of ^{15}N-Labeled *p*-Toluenesulfonamide. The resonances of *p*-toluenesulfonamide and its anion in Figure 1 are observed only because these materials have become enriched with ^{15}N. No ^{15}N signal was observed with a natural-abundance sample of *p*-toluenesulfonamide in dimethyl sulfoxide at a concentration and with an acquisition time comparable to the spectrum in Figure 1c.

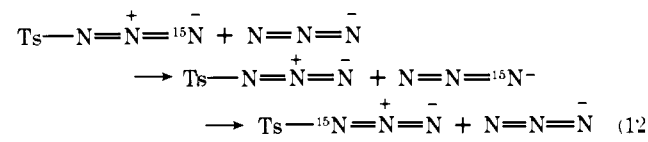
Formation of ^{15}N-labeled *p*-toluenesulfonamide and its anion is not consistent with the equilibrium of eq 6, although the same sequence of reactions with **1**-*1*-^{15}N would lead to labeled *p*-toluenesulfonamide (eq 11). However, there are two pathways leading to the formation of **1**-*1*-^{15}N which will be discussed in the following sections.



(11)

Exchange of Azide Ion. The first route for **1**-*1*-^{15}N formation is associated with the direct nucleophilic attack of azide ion on **1**. A ^{15}N spectrum of sodium azide and **1**-*3*-^{15}N in dimethyl sulfoxide showed signals due to **1**-*3*-^{15}N, **1**-*1*-^{15}N, and sodium azide-*1*-^{15}N, indicating fast azide exchange[25] (eq 12). Similar exchanges have been recently reported by Holm and co-workers[26] with ^{15}N-labeled sodium azide and benzoyl azide in aqueous ethanol.

Azido Transfer to Azide Ion. In solutions of **1**-*3*-^{15}N and sodium azide in dimethyl sulfoxide, two small ^{15}N resonances

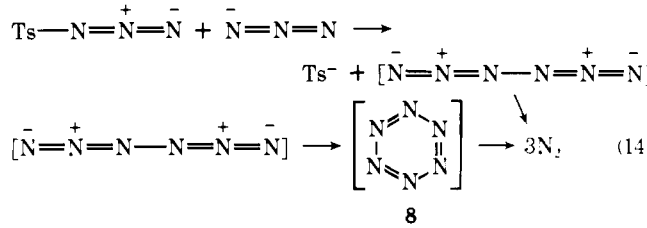


(12)

appear at 24.1 and 64.1 ppm after many hours. The resonance at 64.1 ppm can be attributed to ^{15}N-labeled dinitrogen,[27] because in solutions of *p*-toluenesulfonamide anion and **1**-*3*-^{15}N this signal disappears on purging with dry, unlabeled nitrogen and then slowly reappears over several hours. We propose that dinitrogen is evolved in an unusual reaction in which **1** formally transfers an azido group to azide ion[28,29] (eq 13).

$$TsN_3 + N_3^- \rightarrow Ts^- + 3N_2 \quad (13)$$

Several mechanisms for this slow transformation may be envisioned. The simplest involves a straightforward nucleophilic coupling of **1** and azide ion to give the unknown free pseudohalogen $(N_3)_2$[30,31] which could decompose directly to $3N_2$ or else cyclize to hexazine[32] (**8**) before decomposing (eq 14). Alternatively, intermediates similar to those proposed in the coupling of azide ion with aryldiazonium salts could be involved.[33,34] Distinction between the mechanisms of eq 14 and 15 by ^{15}N labeling is possible if the formation of **9** were reversible (eq 16). However, the ^{15}N spectrum of potassium azide-*1*-^{15}N and **1** in dimethyl sulfoxide after 8 h showed no scrambling of the potassium azide, and this result therefore excludes pentazole reversibility but not irreversible formation of **9**.



(14)

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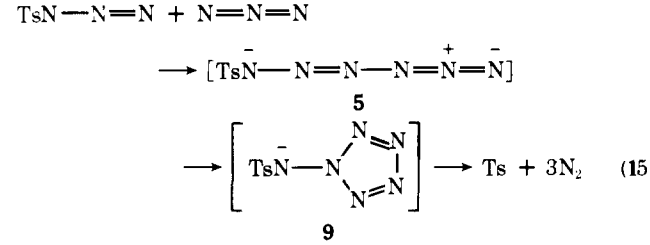
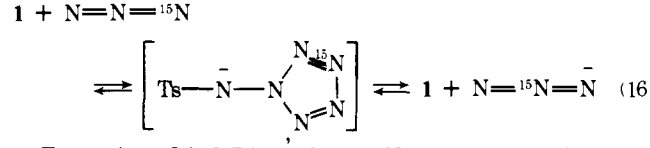


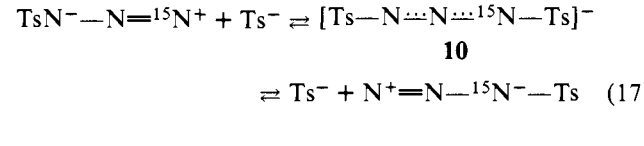
(15)

9



(16)

Formation of 1, 2-Di-*p*-toluenesulfonyltriazene Anion. The second route which interconverts **1**-*3*-^{15}N to **1**-*1*-^{15}N involves *p*-toluenesulfinate anion, formed in the reaction of eq 13 by way of a degenerate azido transfer with **1** through the intermediate triazene, **10** (eq 17). The ^{15}N NMR of **1**-*3*-^{15}N in the presence of small concentrations of the sodium salt of *p*-toluenesulfinic acid (dihydrate) in dimethyl sulfoxide shows that reaction 17 occurs readily. Both **1**-*3*-^{15}N and **1**-*1*-^{15}N are visible in about equimolar amounts within 4 h. Thus, reaction 17 as well as reaction 12 allows for the formation of **1**-*1*-^{15}N from **1**-*3*-^{15}N.



(17)

10

If an excess of the sulfinate salt is added to **1**-*3*-^{15}N in dimethyl sulfoxide, a concentration of the triazene salt, **10**, results. Thus, the ^{15}N NMR of multilabeled **1** with an excess of the sulfinate salt (as the dihydrate) in dimethyl sulfoxide showed that no **1** remained, and only ^{15}N signals attributed to N1 (24.2 ppm) and N2 (−160.3 ppm) of **10** were observed,[35] The ^{15}N spectrum of a concentrated solution of multilabeled **1** and sodium azide in dimethyl sulfoxide after the gas evolution has stopped also shows the resonances of **10** (Figure 2). In addition, Figure 2 shows that the azide ion becomes ^{15}N labeled in accord with eq 12, and, in agreement with eq 13, the resonances of a small amount of labeled dinitrogen are visible.

Cleavage of 1, 3-Di-*p*-toluenesulfonyltriazene in Acid. Both diaryl- and 1-arylsulfonyl-2-aryltriazene are cleaved by acids to an aryldiazonium salt and an amine[36] (eq 18 and 19). In

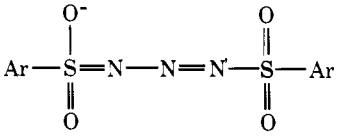
$$ArN(H)-N=N-Ar \overset{H^+}{\rightleftharpoons} ArNH_2-N=N-Ar \longrightarrow ArNH_2 + ArN_2^+ \quad (18)$$

$$ArSO_2N(H)-N=N-Ar \overset{H^+}{\rightleftharpoons} ArSO_2NH_2-N=N-Ar \longrightarrow ArSO_2NH_2 + ArN_2^+ \quad (19)$$

contrast, the ^{15}N NMR of a solution of **10** (generated in situ by addition of the sodium salt of *p*-toluenesulfinic acid to **1**-*3*-^{15}N in dimethyl sulfoxide), acidified with trifluoroacetic acid or acetic acid, shows that **10** decomposes into scrambled **1** and the sulfinic acid (eq 20). This decomposition is somewhat

$$[ArSO_2N\cdots N\cdots NSO_2Ar]^- \xrightarrow{H+} ArSO_2H + N_3SO_2Ar \quad (20)$$

analogous to the base-catalyzed decomposition of 1-arylsulfonyl-3-aryltriazenes to aryl azide and sulfinate salts.[36b] The unusual behavior of **10** is likely to be a consequence of the increased basicity of the sulfonyl oxygens, because of dominant resonance structures such as **11.**



11

Conclusions

The reactions of **1**-*3*-^{15}N with several nucleophiles in dimethyl sulfoxide studied here by ^{15}N NMR enlarge the scope of *p*-toluenesulfonyl azide reactivity and impose limitations on the utility of this reagent. The 2,3 scrambling of **1** by *p*-toluenesulfonamide anion indicates that completely specific ^{15}N labeling of diazo compounds with **1**-*3*-^{15}N may be difficult, if not impossible. Indeed, if **1**-*3*-^{15}N had been employed to synthesize diazocyclopentadiene by the classic route of Doering and DePuy,[37] using the lithium salt of cyclopentadiene, completely ^{15}N-scrambled diazocyclopentadiene would surely have resulted. Furthermore, the sequestering of *p*-toluenesulfonyl azide by *p*-toluenesulfinate anion (**5**) requires that the yields of azido-transfer reactions using **1** must be poor, as has been observed.

Many of the reactions of **1** with nucleophiles may be rationalized by initial formation of adducts similar to those arising from aryldiazonium salts with the same nucleophiles. Viewing **1** as an *N*-diazonium group can be expected to be fruitful for predicting as yet unknown reactions of **1** with other nucleophiles. Clearly, ^{15}N NMR is a useful tool to assist in the unraveling of the general mechanistic course of *p*-toluenesulfonyl azide reactions, and further applications to related systems are in progress.

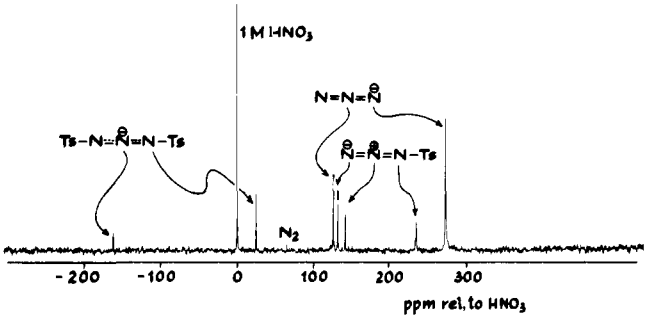


Figure 2. ^{15}N spectrum of 1.2×10^{-2} mol of scrambled *p*-toluenesulfonyl azide (*1*-^{15}N, *2*-^{15}N, *3*-^{15}N) and 1.2×10^{-3} mol of sodium azide in 25 mL of dry dimethyl sulfoxide. The spectrum was begun 53 h after sample preparation, 20-μs pulse angle, 10-s repetition rate, 1949 transients.

Experimental Section

The ^{15}N NMR spectra were taken at 18.25 MHz with a Bruker WH-180 spectrometer, using 15–25-mL samples in 25-mm sample tubes. A 5-mm concentric tube containing a solution prepared by dissolving sufficient $H^{15}NO_3$ in D_2O to give a 1 M acid concentration provided lock and reference signals. Chemical shifts are reported in parts per million upfield from external HNO_3. All spectra were proton coupled, and observations were made at ambient probe temperature, which was approximately 22 °C.

Unless otherwise specified, dimethyl sulfoxide was dried before use by distillation over calcium hydride. *p*-Toluenesulfonyl azide was obtained from *p*-toluenesulfonyl chloride and sodium azide in ethanol, following the procedure of Curtius.[38] Di-*p*-toluenesulfonamide and its sodium salt were prepared according to the method of Dykhanov[23] with *p*-toluenesulfonamide and *p*-toluenesulfonyl chloride in aqueous sodium hydroxide.

***p*-Toluenesulfonyl azide-*3*-^{15}N (1-*3*-^{15}N)** was prepared by diazotization of *p*-toluenesulfonyl hydrazide with 30.2% enriched sodium nitrite, following the method of Curtius.[38] The report of Clusius and Weisser[39] that a similar preparation of phenyl azide-*3*-^{15}N resulted in the formation of 2–7% of phenyl azide-*2*-^{15}N made it necessary to determine if the labeling of **1** was completely specific. A ^{15}N spectrum of **1**-*3*-^{15}N in dimethyl sulfoxide indicated that within the limits of detection (~0.5%) only N3 was ^{15}N labeled. It was found that **1**-*3*-^{15}N maintains its isotopic integrity in dimethyl sulfoxide for at least 34 h; however, after 2 weeks, approximately 20% of **1**-*1*-^{15}N is found.

Sodium Salt of *p*-Toluenesulfonamide. A mixture of *p*-toluenesulfonamide and the sodium salt of *p*-toluenesulfonamide in dimethyl sulfoxide was generated in situ by the slow addition of an excess of *p*-toluenesulfonamide in dimethyl sulfoxide to a stirred solution of dimsyl anion under nitrogen. Dimsyl anion was prepared by treating dimethyl sulfoxide with sodium hydride (50% oil suspension) as described by Corey and Chaykovsky.[40] After addition of *p*-toluenesulfonamide to the dimsyl anion, the solution was stirred for 2.5 h at 60 °C under nitrogen. This solution was cooled to room temperature before use in the ^{15}N experiments. The ^{15}N NMR spectrum of *p*-toluenesulfonamide and **1**-*3*-^{15}N in dimethyl sulfoxide showed that *p*-toluenesulfonamide itself does not scramble the ^{15}N label in *p*-toluenesulfonyl azide, even after 3 days.

Isolation of a Mixture of 1-, 2-, and 3-^{15}N-Labeled *p*-Toluenesulfonyl Azides. Dimethyl sulfoxide solutions of ^{15}N-labeled *p*-toluenesulfonyl azide scrambled by *p*-toluenesulfonamide anion or azide ion were combined. After addition of water to the solution, it was extracted three times with pentane. The combined pentane extracts were washed three times with water and dried first over anhydrous sodium sulfate, then over calcium sulfate. The solvent was removed under reduced pressure, and the ^{15}N spectrum of the residual mixture of ^{15}N-labeled *p*-toluenesulfonyl azides showed that no other ^{15}N-labeled compounds were present.

Reactions of Di-*p*-toluenesulfonamide with Sodium Azide. Di-*p*-toluenesulfonamide (5.5 g, 0.017 mol) and 3.0 g (0.46 mol) of sodium azide were added to 80 mL of dimethyl sulfoxide. The mixture was stirred at room temperature for 4 days. After addition of 400 mL of water, the solution was extracted with pentane. The combined extracts

were washed twice with water and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The remaining faint-yellow residue was dissolved in ether and an ethereal solution of triphenylphosphine was added. No *p*-toluenesulfonyl azide–triphenylphosphine adduct could be isolated.[41]

References and Notes

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(15) Clusius, K.; Weisser, H. R. *Helv. Chim. Acta* **1952,** *35*, 1524–1527.
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(20) The ^{15}N chemical shift of potassium azide-*1*-^{15}N (96.8%) in dimethyl sulfoxide is 270.0 ppm. A natural-abundance ^{15}N spectrum of sodium azide in water gives chemical shifts for N1 of 275.8 ppm and for N2 of 127.0 ppm. These ^{15}N chemical shifts are in general agreement with the reported ^{14}N chemical shifts: Beck, W.; Becker, W.; Chew, K. F.; Derbyshire, W.; Logan, N.; Revitt, D. M.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1972,** 245–247.
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(22) Anselme and co-workers have noted analogous side reactions.[11] Thus, diazo transfer of **1** to benzylamine anion resulted in some formation of *N*-benzyl-*p*-toluenesulfonamide. Displacement of the *p*-toluenesulfonamide group by azide ion could not be accomplished.[11]
(23) Dykhanov, N. N. *Zh. Obshch. Khim.* **1959,** *29*, 3563–3566.
(24) The ^{15}N NMR of natural-abundance *p*-toluenesulfonamide in undried dimethyl sulfoxide shows a triplet at 279.3 ppm with an 81-Hz coupling constant, in agreement with the triplet seen in Figure 1c. The ^{15}N NMR of an equimolar mixture of *p*-toluenesulfonamide and its anion in dimethyl sulfoxide shows a singlet at 273.1 ppm. This indicates that very little of the *p*-toluenesulfonamide anion remains, even after a few hours with **1.**
(25) After about 1.5 h, the scrambling of **1**-*3*-^{15}N (see Figure 1a) proceeded to ~25% of completion. Many days later, this scrambling was complete. See also ref 13.
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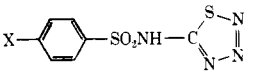

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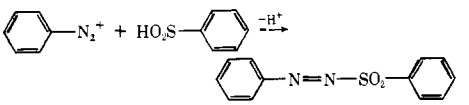

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